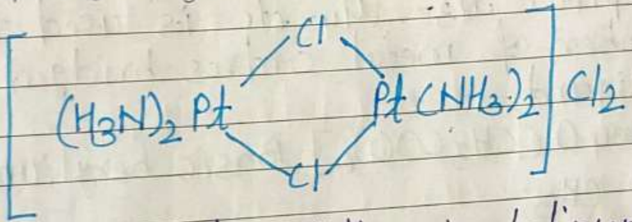
IUPAC Names of Bridged Polynuclear Complexes.

1. Ligand that bridges two metal cations or atoms is denoted by prefix μ- added to the name of the bridging ligand. e.g.

$[(H_3N)_5Cr-O-Cr(NH_3)_5]^{4+}$

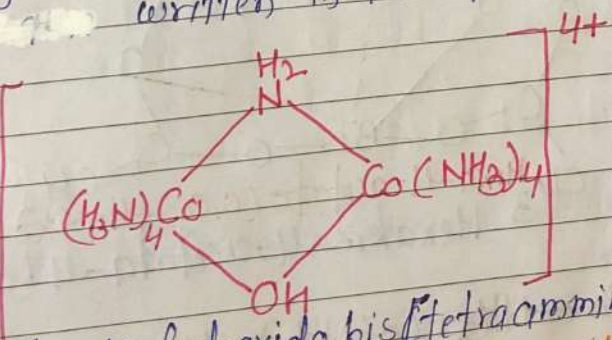
μ- oxidobis[pentaamminechromium(III)]

2. If a complex has 2, 3 or 4 bridging ligands of same kind then prefix di-μ, tri-μ, tetra-μ are used raspectively. e.g.

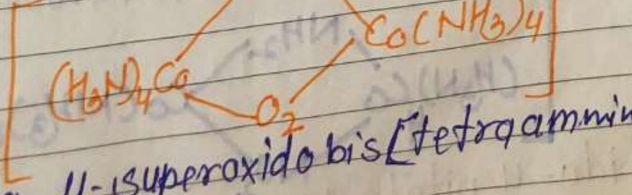


di-μ- chloridobis[diammineplatinum(II)] chloride

3. If a complex has 2 or more different kind of ligands, then prefix μ is used for each kind of bridging ligand. The name of the bridging ligands are written in the alphabetical order. e.g.

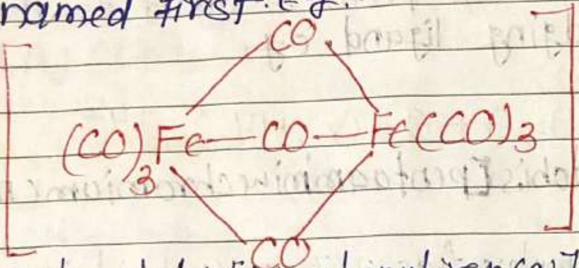


μ-amido-μ- hydroxido bis[tetraamminecobalt(III)]



μ-amido-μ-superoxido bis[tetraammine cobalt(III)]

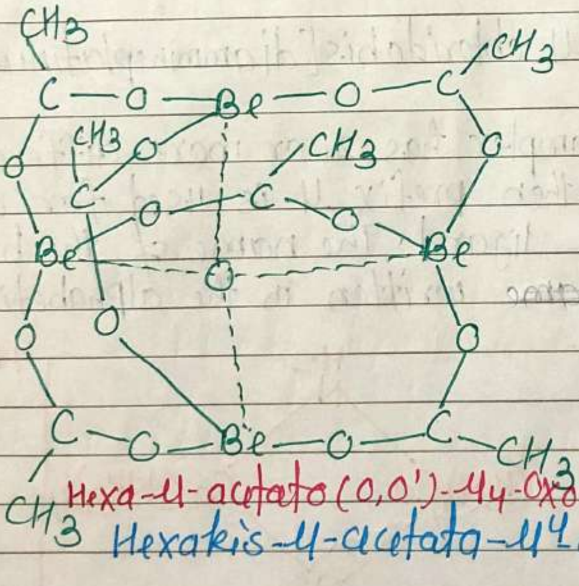
4. If the bridging and the terminal ligands both are of same kind then the bridging ligands are named first. e.g.



Tri-μ-carbonyl bis[tricarbonyliron(0)]

5. If a bridging ligand bridges more than two metal centres prefix μ_3-, μ_4- etc is used to indicate the number of metal centres bridged with a given ligand.

e.g. $[Be_4O(CH_3COO)_6]$ Basic beryllium acetate.

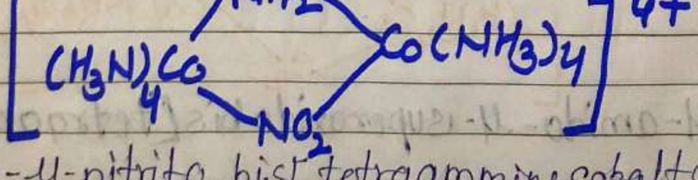


Hexa-μ-acetato(O,O')-μ_4-oxo tetraberyllium(II)

Hexakis-μ-acetato-μ^4 oxido tetraberyllium(II)

$[(H_3N)_5Co—NH_2—Co(NH_3)_4(H_2O)]Cl_5$

Pentaammine cobalt(III)-μ-amido tetraammine aqua cobalt(III) chloride.



μ-amido-μ-nitrito bis[tetraammine cobalt(III)]

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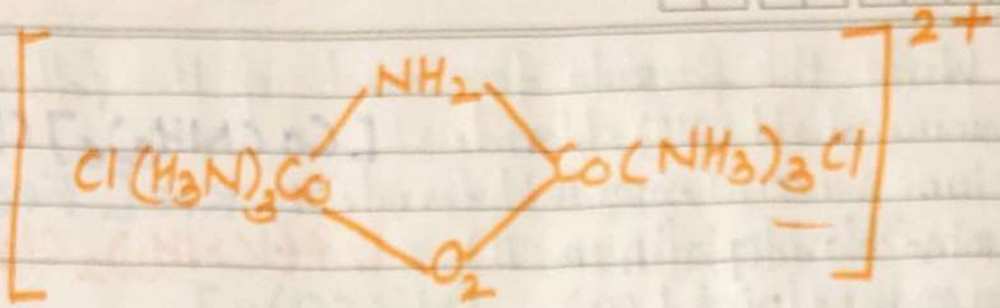
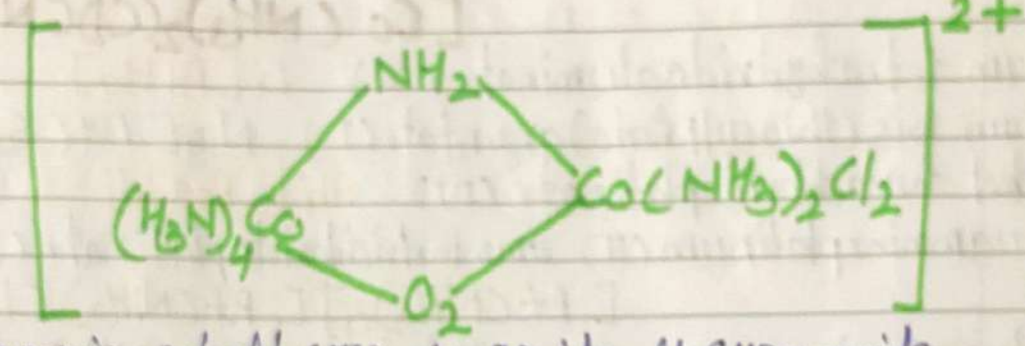
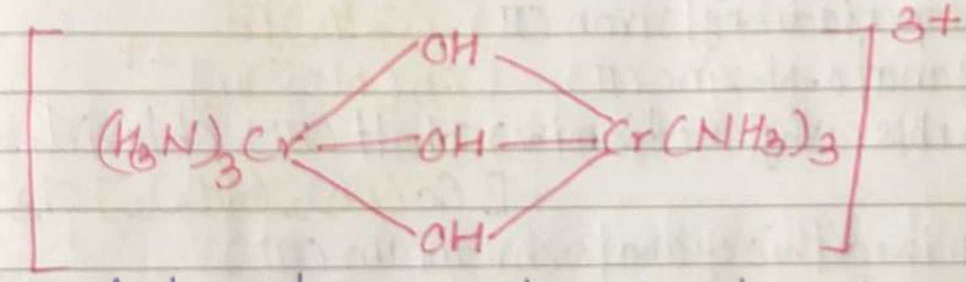


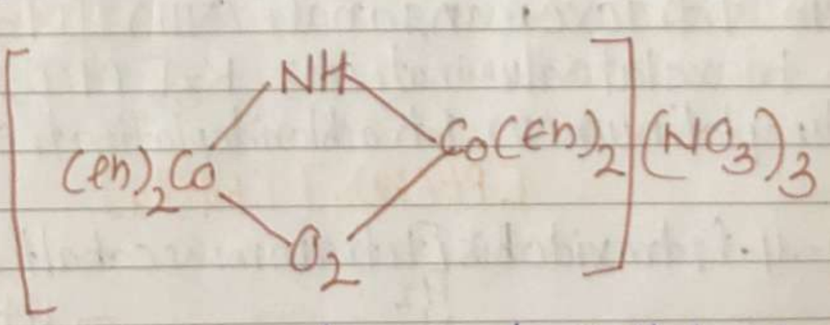
μ-amido-μ-superoxido bis[triamminechloridocobalt(III)]



Tetraammine cobalt(III)-μ-amido-μ-superoxido-diamminedichloridocobalt(III)



tri-μ-hydroxido-bis[triamminechromium(III)]



μ-imido-μ-superoxido tetrakis[ethylenediaminecobalt(III) nitrate.

Write the formula for each of the following complexes:

Hexamminecobalt (III) chloride $[Co(NH_3)_6]Cl_3$

Potassium iron(III) hexacyanidoferrate(II) $KFe[Fe(CN)_6]$

Diamminedichloridoplatinum (II) $[Pt(NH_3)_2Cl_2]$

Tetracarbonylnickel (0) $[Ni(CO)_4]$

Triamminechloridocyanidonitritocobalt(III)

$[Co(NH_3)_2(Cl)CN(NO_2)]$

Lithium tetrahydridoaluminate (III) $Li[AlH_4]$

Sodium bis(thiosulphato)argentate(I) $Na_3[Ag(S_2O_3)_2]$

Nickel hexachloridoplatinate (IV) $Ni[PtCl_6]$

Tetraammineplatinum(II) amminetrichloridoplatinate (II)

$[Pt(NH_3)_4][Pt(NH_3)Cl_3]$

Tetraamminecopper (II) sulphate. $[Cu(NH_3)_4]SO_4$.

Potassium tetracyanidonickelate(0) $K_4[Ni(CN)_4]$

bis(cyclopentadienyl)iron (II) $(C_5H_5)_2Fe$

tetracyanato-N-zinc (II) $[Zn(NCS)_4]^{2+}$

diamminebis(ethylenediamine)cobalt (III) chloride.

$[Co(en)_2(NH_3)_2]Cl_3$

Tetraamminedithiocyanatochromium (III)

$[Cr(NH_3)_4(SCN)_2]^+$

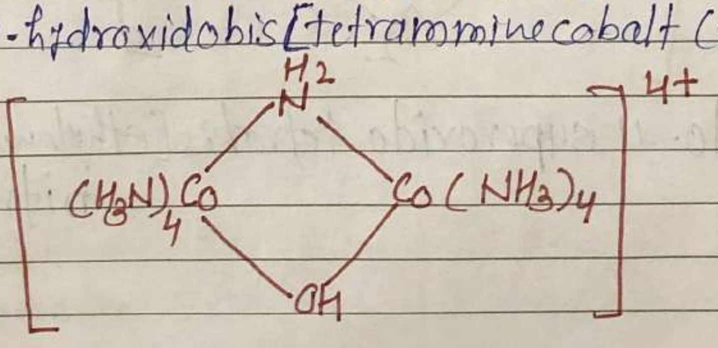
Potassium tetraoxomanganate (VII) $[MnO_4]^-$

Potassium trioxalatoaluminate (III) $K_3[Al(C_2O_4)_3]$

Tetrapyridineplatinum (II) tetrachloridoplatinate (II)

$[Pt(Py)_4][PtCl_4]$

μ-amido-μ-hydroxidobis[tetramminecobalt (III)]

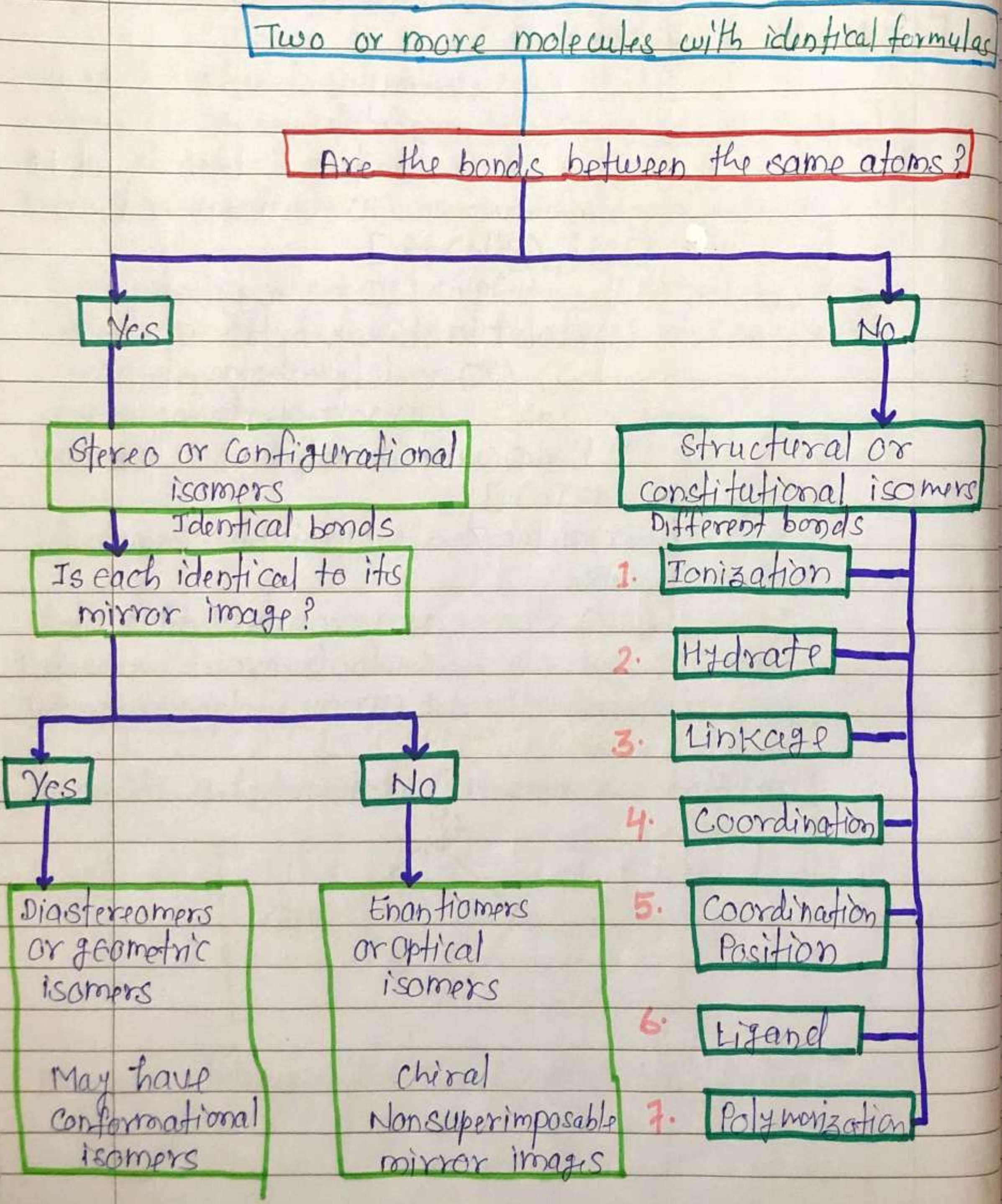


Ammonium tetrachloridoruthenate (~~II~~) $(NH_4)[RuCl_4]^-$

Isomerism

compounds that have the same chemical formula but different structural arrangements are called isomers.

Phenomenon of existence of isomers is called isomerism.



Structural Isomerism (Constitutional isomerism)

- Isomers that have different atom to atom bonding are called structural isomers.
- structural isomerism arises due to different bonding between metal and ligands.

1. Ionization Isomerism:

This type of isomerism is arises due to the exchange of ligands between the complex ion (coordination sphere) and the ions outside it (ionization sphere or counter ion).

- These isomers give different ions in aqueous solution and shows different properties.

$[Co(NH_3)_5Br]SO_4$ & $[Co(NH_3)_5SO_4]Br$

Red-violet Red

$$[Co(NH_3)_5Br]SO_4 \xrightarrow{Ba^{2+}} [Co(NH_3)_5Br]^{2+} + BaSO_4$$

white ppt.

$$[Co(NH_3)_5Br]SO_4 \xrightarrow{Ag^+} \text{No precipitate}$$

$$[Co(NH_3)_5SO_4]Br \xrightarrow{Ag^+} [Co(NH_3)_5SO_4]^+ + AgBr$$

Cream Coloured ppt

$$[Co(NH_3)_5SO_4]Br \xrightarrow{Ba^{2+}} \text{No ppt.}$$

other examples of ionization sphere:

$[Pt(NH_3)_4Cl_2]Br_2$ & $[Pt(NH_3)_4Br_2]Cl_2$

$[Co(en)_2NO_2 \cdot Cl]SCN$, $[Co(en)_2NO_2 \cdot SCN]Cl$ &
$[Co(en)_2Cl \cdot SCN]NO_2$

$[Co(NH_3)_5Cl]SO_4$ & $[Co(NH_3)_5SO_4]Cl$

$[Co(NH_3)_5(NO_3)]SO_4$ & $[Co(NH_3)_5(SO_4)]NO_3$

2. Hydrate Isomerism:

- when water molecules are exchanged between coordination sphere and ionization sphere, the resulting isomers are called hydrate isomers.

eg. 1. $CrCl_3 . 6H_2O$

$[Cr(H_2O)_6]Cl_3$ violet

$[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$ Bright blue green

$[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$ dark green

$[Cr(H_2O)_3Cl_3] \cdot 3H_2O$ dark green.

2. $[Co(NH_3)_4(H_2O)Cl]Br_2$ and $[Co(NH_3)_4Br_2]Cl \cdot H_2O$
3. $[Co(NH_3)_5(H_2O)](NO_3)_3$ and $[Co(NH_3)_5NO_3](NO_3)_2 \cdot H_2O$

Note: Hydrate isomerism is also a kind of ionization isomerism.

Chemical Test for Identification of Hydrate Isomerism:

I. e.g.

when reacted with Ag^+ ions.

$$[Cr(H_2O)_6]Cl_3 \xrightarrow{3Ag^+} [Cr(H_2O)_6]^{3+} + \underset{\text{white ppt}}{3AgCl}$$

$$[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O \xrightarrow{2Ag^+} [Cr(H_2O)_5Cl]^{2+} \cdot H_2O + \underset{\text{white ppt}}{2AgCl}$$

$$[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O \xrightarrow{Ag^+} [Cr(H_2O)_4Cl_2] \cdot 2H_2O + \underset{\text{white ppt}}{AgCl}$$

II. Rx^n with conc. H_2SO_4:

$$[Cr(H_2O)_6]Cl_3 \xrightarrow{H_2SO_4} [Cr(H_2O)_6]Cl_3$$

Does not loses water molecule with H_2SO_4.

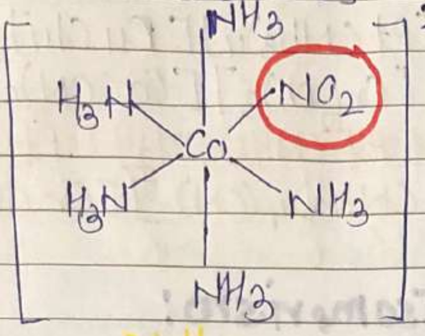
$$[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O \xrightarrow{H_2SO_4} [Cr(H_2O)_5Cl]Cl_2 + H_2O$$

$$[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O \xrightarrow{H_2SO_4} [Cr(H_2O)_4Cl_2]Cl + 2H_2O$$

3. **Linkage Isomerism:** This type of isomerism is arises when an ambidentate ligand can coordinate to a metal cation through either of the two different donor atoms.

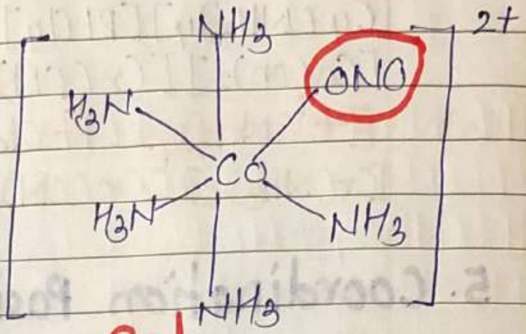
e.g. $[Co(NH_3)_5NO_2]^{2+}$ and $[Co(NH_3)_5ONO]^{2+}$

i)



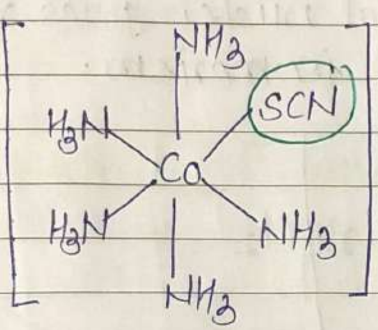
Yellow

and

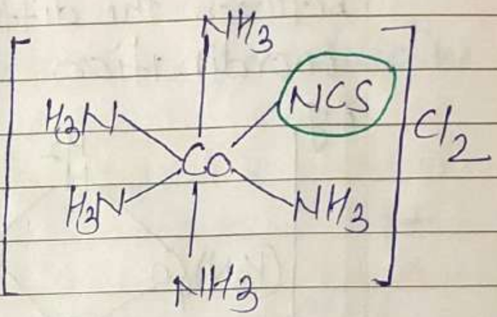


Red

ii)



Cl_2 and



iii) $[Co(en)_2(NO_2)_2]^+$ and $[Co(en)_2(ONO)_2]^+$

iv) $[Pd(PPh_3)_2(SCN)_2]$ and $[Pd(PPh_3)_2(NCS)_2]$

Note: Generally CN^- does not behaves as an ambidentate ligand. It always bonds through the carbon atom because of the stronger π-bonding via carbon donation.

e.g. where CN^- acts as ambidentate ligand.
cis$[Co(trien)(CN)_2]^+$ and cis $[Co(tren)(NC)_2]^+$
Prussian & turnbull blue.
$\cdots \overset{II}{Fe}-CN-\overset{III}{Fe}-NC-\overset{II}{Fe}-CN-\overset{III}{Fe}-NC-\overset{II}{Fe}\cdots$

4. Coordination Isomerism:

→ When both the positive and negative ions are complex ions, there may be exchange of ligands between these two complex ions resulting in coordination isomers.

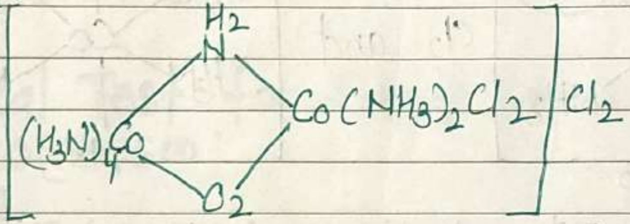
→ In the pairs of these isomers the central metal cation in the two coordination sphere may be same or different.

E.g. $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$
$[Cu(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_4][CuCl_4]$
$[Co(en)_3][Cr(CN)_6]$ and $[Cr(en)_3][Co(CN)_6]$
$[Pt^{II}(NH_3)_4][Pt^{IV}Cl_6]$ and $[Pt^{IV}(NH_3)_4Cl_2][Pt^{II}Cl_4]$
$[Cr(NH_3)_6][Cr(CN)_6]$ & $[Cr(NH_3)_4(CN)_2][Cr(NH_3)_2(CN)_4]$

5. Coordination Position Isomerism:

In polynuclear complexes an interchange of ligands between the different metal nuclei gives rise to coordination positional isomerism.

E.g.



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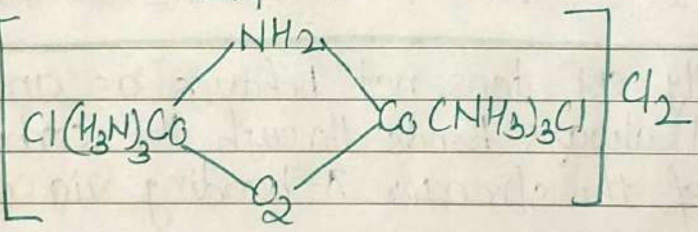

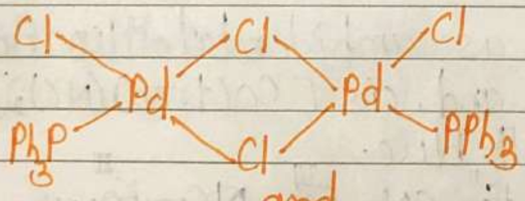

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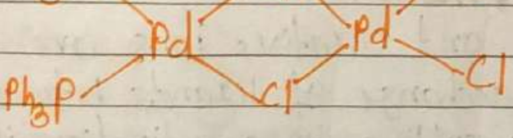
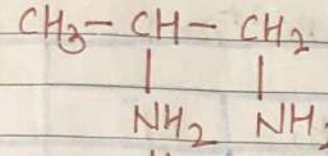


6. Ligand Isomerism:

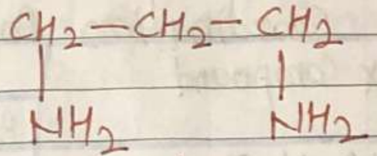
If a ligand itself exists in two or more isomeric forms, then the complexes containing such ligands also exist in isomeric forms.

e.g. i)



$CH_3-\underset{NH_2}{\underset{|}{CH}}-\underset{NH_2}{\underset{|}{CH_2}}$

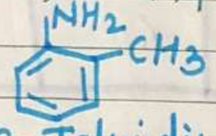
1,2-diaminopropane(pn)



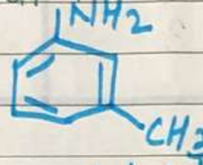
$\underset{NH_2}{\underset{|}{CH_2}}-CH_2-\underset{NH_2}{\underset{|}{CH_2}}$

1,3-diaminopropane. (tn)

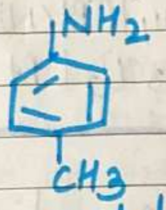
ii) o-, m- and p-toluidine.



o-Toluidine.

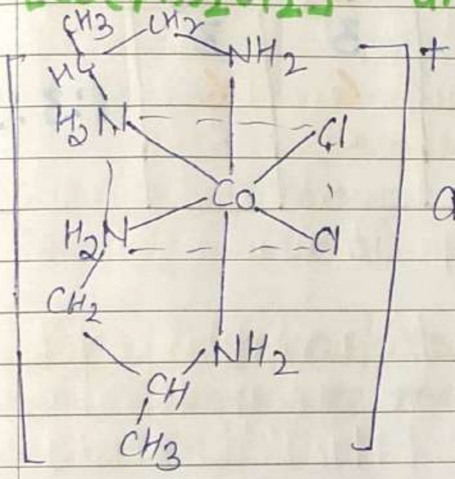


m-toluidine



p-toluidine

$[Co(pn)_2Cl_2]^+$ and $[Co(tn)_2Cl_2]^+$



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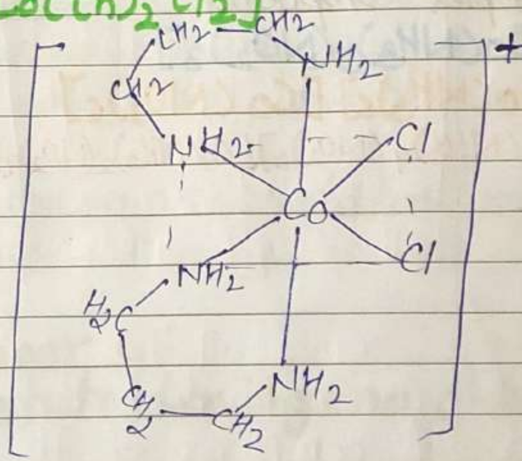
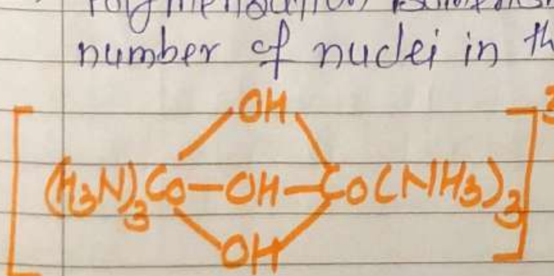


7. Polymerization Isomerism:

This is not a true isomerism because it occurs between compounds having same empirical formula, but different molecular weights.

→ Thus $[Pt(NH_3)_2Cl_2]$, $[Pt(NH_3)_4][PtCl_4]$, $[Pt(NH_3)_4][Pt(NH_3)Cl_3]_2$ and $[Pt(NH_3)_3Cl]_2[PtCl_4]$ all have the same empirical formula.

→ Polymerization isomerism may be due to a different number of nuclei in the complex. e.g.



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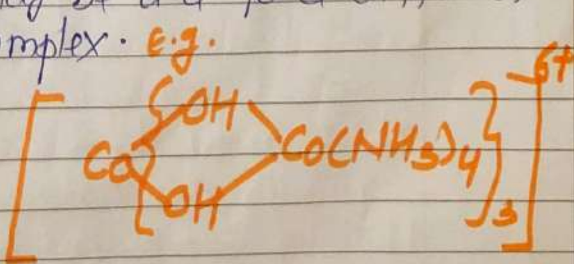

Coordination Polymers of Pt^{2+} ion:

Complex compound	Number of			Ratio
	Pt^{2+}	NH_3	Cl^-	
$[Pt(NH_3)_2Cl_2]$	1	2	2	1:2:2
$[Pt(NH_3)_4][PtCl_4]$	2	4	4	
$[Pt(NH_3)_4][Pt(NH_3)Cl_3]_2$	3	6	6	
$[Pt(NH_3)_3Cl]_2[PtCl_4]$	3	6	6	

Coordination polymers of Co^{3+} ion

Complex compound	No. of			Ratio
	Co^{3+}	NH_3	NO_2^-	
$[Co(NH_3)_3(NO_2)_3]$	1	3	3	1:3:3
$[Co(NH_3)_6][Co(NO_2)_6]$	2	6	6	
$[Co(NH_3)_4(NO_2)_2][Co(NH_3)_2(NO_2)_4]$	2	6	6	